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N INTRODUCTION

EDITION

Malcolm P. Stevens

THIRD EDITION

# POLYMER CHEMISTRY

AN INTRODUCTION

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New York Oxford

OXFORD UNIVERSITY PRESS

1999

referred to as the *repeating unit* (or *monomeric unit*). One might reasonably argue that the first repeating unit shown previously is  $-\text{CH}_2-$  rather than  $-\text{CH}_2\text{CH}_2-$ ; however, it is more conventional to define repeating units in terms of monomer structure. The *smallest* possible repeating unit ( $-\text{CH}_2-$  in this instance) is referred to as the *base unit*.

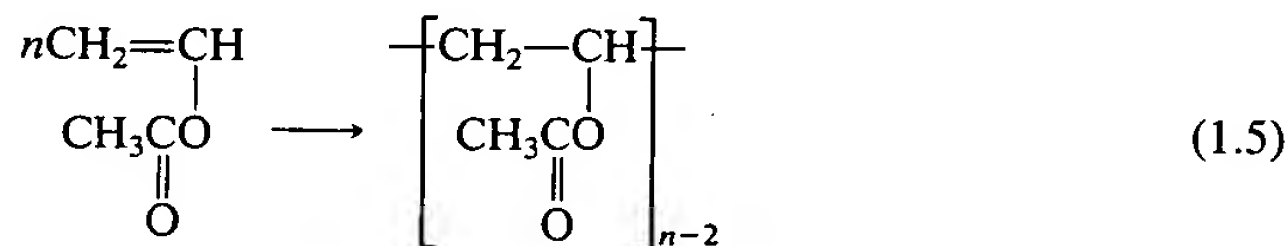
*End groups* are the structural units that terminate polymer chains. Where end groups are specified, they are shown outside the brackets, for example,



Some polymers are deliberately synthesized with reactive end groups for undergoing further reaction. Polymers containing reactive end groups are called *telechelic polymers* (from the Greek *tele*, far, and *chele*, claw). Related to telechelic polymers are the commercially important *reactive oligomers*, which are oligomers containing end groups capable of undergoing polymerization, usually by heating, to form network polymers.

Polymers formed by alkene addition reactions are called *homochain* polymers because the polymer chain, or *backbone*, as it is commonly called, consists of a single atom type—carbon—with other atoms or groups of atoms attached. *Heterochain* polymers such as polyethers or polyesters contain more than one atom type in the backbone.

The *degree of polymerization* (DP) refers to the total number of structural units, including end groups, and hence is related to both chain length and molecular weight. Consider, for example, the polymerization of vinyl acetate (an important industrial monomer) in reaction (1.5):



DP in this case is equivalent to  $n$  (note that two monomer units are at the chain ends), and the molecular weight of the macromolecule is the product of DP and the molecular weight of the structural unit. For a DP of 500, for example,

$$\text{Molecular weight} = 500 \times 86 = 43,000$$

Because polymer chains within a given polymer sample are almost always of varying lengths (except for certain natural polymers like proteins), we normally refer to the *average degree of polymerization* (DP).

A polymer prepared from a single monomer is called a *homopolymer*. If two or more monomers are employed, the product is a *copolymer*. In copolymers the monomeric units may be distributed randomly (*random copolymer*), in alternating fashion (*alternating copolymer*), or in blocks (*block copolymer*). A *graft copolymer* consists of one polymer branching from the backbone of the other. These various possibilities are illustrated schematically in Figure 1.1 for hypothetical monomers A and B. There are different kinds of block copolymers. Where blocks of A and B alternate in the backbone, the polymer is designated an  $-\text{AB}-$  *multiblock* copolymer. If the backbone consists of a single block of each, it is an *AB diblock* copolymer. Other possibilities include ABA (triblock: a central B block with terminal A blocks) and ABC (triblock: one each of three different blocks). As will be seen later, certain monomer combinations display a tendency toward alternation during copolymerization, whereas formation of block and graft copolymers requires special techniques. Polyesters



TABLE 7.1. Commercially Important Polymers Prepared by Ionic Polymerization

Polymer or Copolymer	Major Uses
<b>Cationic<sup>a</sup></b>	
Polyisobutylene and polybutenes <sup>b</sup> (low and high molecular weight)	Adhesives, sealants, insulating oils, lubricating oil and grease additives, moisture barriers
Isobutylene-isoprene copolymer <sup>c</sup> ("butyl rubber")	Inner tubes, engine mounts and springs, chemical tank linings, protective clothing, hoses, gaskets, electrical insulation
Isobutylene-cyclopentadiene copolymer	Ozone-resistant rubber
Hydrocarbon <sup>d</sup> and polyterpene resins	Inks, varnishes, paints, adhesives, sealants
Coumarone-indene resins <sup>e</sup>	Flooring, coatings, adhesives
Poly(vinyl ether)s	Polymer modifiers, tackifiers, adhesives
<b>Anionic<sup>f</sup></b>	
<i>cis</i> -1,4-Polybutadiene	Tires
<i>cis</i> -1,4-Polyisoprene	Tires, footwear, adhesives, coated fabrics
Styrene-butadiene rubber (SBR) <sup>g</sup>	Tire treads, belting, hose, shoe soles, flooring, coated fabrics
Styrene-butadiene block and star copolymers	Flooring, shoe soles, artificial leather, wire and cable insulation
ABA block copolymers (A = styrene, B = butadiene or isoprene)	Thermoplastic elastomers
Polycyanoacrylate <sup>h</sup>	Adhesives

<sup>a</sup>AlCl<sub>3</sub> and BF<sub>3</sub> most frequently used coinitiators.

<sup>b</sup>"Polybutenes" are copolymers based on C<sub>4</sub> alkenes and lesser amounts of propylene and C<sub>5</sub> and higher alkenes from refinery streams.

<sup>c</sup>Terpolymers of isobutylene, isoprene, and divinylbenzene are also used in sealant and adhesive formulations.

<sup>d</sup>Aliphatic and aromatic refinery products.

<sup>e</sup>Coumarone (benzofuran) and indene (benzocyclopentadiene) are products of coal tar.

<sup>f</sup>*n*-Butyllithium most common initiator.

<sup>g</sup>Contains higher *cis* content than SBR prepared by free radical polymerization.

<sup>h</sup>Monomer polymerized by adventitious water.

Compounds used most frequently to effect cationic polymerization are mineral acids, particularly H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>, and such Lewis acids as AlCl<sub>3</sub>, BF<sub>3</sub>, TiCl<sub>4</sub>, and SnCl<sub>4</sub>. Lewis acids are seldom effective alone; rather they require the presence of trace amounts of water or some other proton or cation source, which, on reaction with the Lewis acid, forms the electrophilic species that initiates polymerization. Examples are the reactions of BF<sub>3</sub> with water (7.2) and aluminum chloride with an alkyl chloride (7.3). Because it is the proton or carbocation that initiates the polymerization reaction, the compounds that give rise to them are correctly referred to as the *initiators*, and the Lewis acids are *coinitiators*.<sup>5</sup> The com-



**Mixing of solid block or block-type copolymer with other solid polymer; mixing of said polymer mixture with a chemical treating agent; mixing of a block or block-type copolymer with specified intermediate condensation product or with specified polymer-forming ingredients; processes of forming or reacting; or the resultant product of any of the above operations:**

This subclass is indented under subclass 55. Subject matter which involves the mixing of a solid block or block-type copolymers with other solid polymer(s); mixing of said polymer mixture with a chemical treating agent; mixing of block or block-type copolymer with a specified intermediate condensation product or with specified polymerforming ingredients or their polymers; or processes of mixing or forming; or the resultant product of any of the above mixtures.

(1) Note. For purposes of classification a polymer is classified as:

(A) A block copolymer when

1. The structure is given, i.e., to a long polymer backbone is attached or coupled to one or both of its terminal ends one or more chemically dissimilar polymers at least three reactant units in length or,

2. the copolymer is named as a block providing that the disclosure is otherwise silent as to its structure or, if the structure is likewise given, it is consistent with that described above or,

3. the structure can be ascertained from the following limiting process conditions:

(a) Treating a nonterminated solid polymer, that is, one which is terminally active or "living", with an ethylenic reactant with subsequent polymerization to form additional blocks. The process may be continued to produce higher order block copolymers. For example, treating dilithiated polystyrene with butadiene to yield an ABA block copolymer.

(b) Two or more chemically dissimilar nonidentical solid polymer chain ends are coupled directly or through the use of a chemical agent. For example, the coupling of hydroxy-terminated solid polybutadiene with hydroxy terminated polyethylene glycol terephthalate using phosgene.

(B) A block-type copolymer when

1. The structure is given, i.e., to a long solid polymer backbone possessing terminally active sites, e.g., contains functional groups or is a "living polymer", etc., is attached or coupled through

chemical reaction with those functional groups or sites an ethylenic reactant containing one or more functional groups or sites, for example, contacting hydroxy terminated polybutadiene with allyl isocyanate or,

2. two or more identical solid polymer chain ends are coupled directly or through the use of a chemical agent. For purposes here, identical means those polymer segments which contain the same backbone but differ (e.g., in stereoregularity, isotacticity syndiotacticity, atacticity, optical activity, or degree of polymerization). Thus, coupling lithium terminated polystyrene segments with molecular weights of 25,000 and 100,000 respectively with stannic chloride is proper for this subclass.

Failure to meet one or more of these requirements, the reaction is considered to produce a polymeric blend. For example, contacting lithium terminated polystyrene with ethylene oxide followed by blending with polyacrylic acid places the product blend in subclass 221.

(2) Note. Patents which describe the aftertreatment of solid polymer from ethylenic reactants only with a nonethylenic agent are classified according to the reactants first leading to formation of the solid polymer. However, if the aftertreating agent is an ethylenic reactant, it is given equal weight with these reactants used in making the solid polymer.

## Nomenclature and Notational Problems in the Phase Separation Characteristics of Block Copolymers

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### Block Copolymer Organizational Nomenclature

The nomenclature related to the chemical structure of block copolymers is relatively well established (1,2). Thus, a diblock copolymer of polybutadiene and polystyrene is written:

polybutadiene-*block*-polystyrene . . . . . (1)

(The reader should note that the use of *-b-* to indicate a block copolymer is out of date; nomenclature such as poly(butadiene-*b*-styrene) should be discouraged.)

Block copolymers come in three main categories: diblock copolymers, as delineated by structure (1) above and sometimes referred to as AB block copolymers, triblock copolymers of the ABA type, and multiblock copolymers of the  $(AB)_n$  type. There are several other types, such as ABC block copolymers containing three different blocks, and the star block copolymers. This last has a central point, with three or more arms, each of which is in the form of a block copolymer, usually of the AB type. Some novel types of block copolymers are discussed by Hadjichristidis and coworkers(3,4), including the 4-miktoarm star quaterpolymer of the ABCD type, and a super-H block copolymer of the  $B_3AB_3$  type. There is also the inverse 4-miktoarm block copolymer of the  $(AB)_2(BA)_2$ , a type of star block copolymer. These latter, newly named by Hadjichristidis, have not been discussed yet by the IUPAC polymer nomenclature committee.

However, there is no formal nomenclature at all relative to phase separation and concomitant morphologies. This *back page* of PMSE will be mostly devoted to a description of current practice, with a few suggestions for use.

### Phase Separation

Most polymer blends exhibit *lower critical solution temperatures* (LCST). This means that the two polymers become more miscible as the temperature is lowered, see Figure 1. Note that the ordinary tie lines of physical chemistry apply here. In Figure 1, the solid line is called the binodal and the dashed line the spinodal(5). These two lines demarcate regions of different kinetics of phase separation. Liquid-liquid phase separation is assumed. If one of the components crystallizes, quite different phase diagrams emerge(6). Occasionally, *upper critical solution temperatures* (UCM) are observed for blends at some lower temperature range. Typical data may be obtained by raising the temperature rapidly from some temperature in the totally miscible range to some higher temperature, and observing changes via optical clarity and microscopy(7). Figure 1 assumes particular molecular weights for the two polymers in question. Different molecular weights result in different positions of the phase diagram, and different maximum temperatures of mutual miscibility. Here, the temperature and the composition of a particular polymer pair is varied.

### The Order-Disorder Transition

The case for block copolymers is significantly different. The molecular weights of the blocks and the overall composition of the block copolymer cannot be varied independently. Therefore, a classical phase



diagram, such as shown in Figure 1, cannot exist, The result has been a plethora of new notation.

Some of the terms used for the temperature of phase separation in block copolymers include the *order-disorder* (ODT) or the microphase separation transition (MST) see Figure 2. In Figure 2,  $\chi Z$  represents the heat of mixing per chain. Other notation in common use is the *narrow interphase approximation* (NIA) which means that one is in the strong segregation regime, i.e., far from the MST(8). Closer to the MST, one speaks of the weak segregation regime(9). At the MST, other people talk about an *upper critical ordering temperature* (UCOT) and a lower critical ordering temperature (LCOT)(10). While most polymer blends exhibit a LCST, most block polymers exhibit an UCOT. An UCOT implies a nucleation and growth mechanism for the kinetics of phase separation. Whether one speaks of a LCST and an UCST or a LCOT and an UCOT, it must be noted that the UCST and UCOT appear at *lower* temperatures than the corresponding LCST and LCOT, respectively.

## Morphology

Most block copolymers are phase separated, that is, the two kinds of blocks are immiscible. (Most of the important properties of block copolymers, including thermoplastic elastomers, elastic fibers, and surfactant applications, depend on phase separation.) The three most common morphologies observed are spheres, cylinders, and lamellae. The appearance of each of these depends on the relative block lengths, see Figure 2(11). Some of the more exotic morphologies include the *ordered, bicontinuous double-diamond* (OBDD)(12), consisting of an interconnected tetrahedral arrangement of short rods, in the form of a double diamond kind of structure. There is also an ABCB block copolymer that forms an *ordered tricontinuous double-diamond* (OTDD) morphology(13), and a ripple or perforated-lamellar morphology of an ill-defined type(14). Semi-crystalline block copolymers often possess a lamellar morphology(15).

A major restriction on all block copolymer morphologies is that the interfaces must be placed relative to one another such that the junction between the blocks can fit easily. There are several other possible morphologies that fit this restriction, the subject of future research. Overall, the whole area of block copolymer phase separation and morphology lacks a coherent and accepted nomenclature, although its great importance is leading to continuous and numerous research programs.

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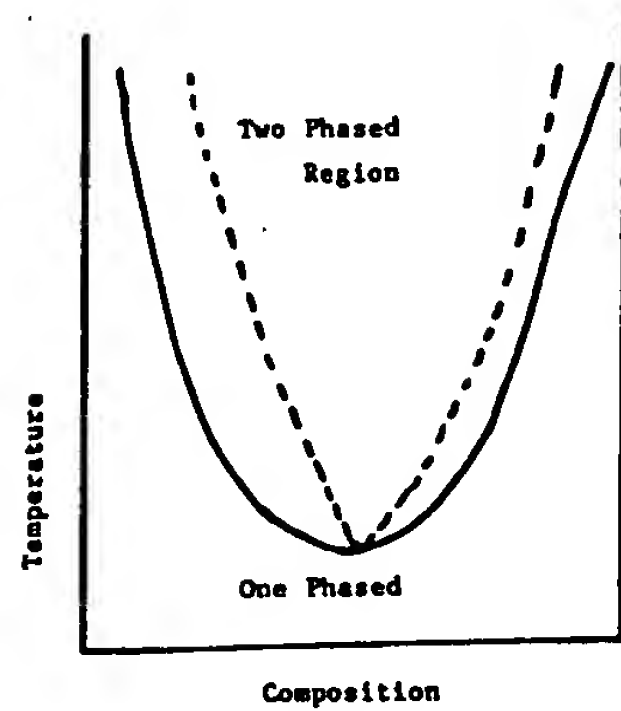


Figure 1. Typical phase diagram for a polymer blend.

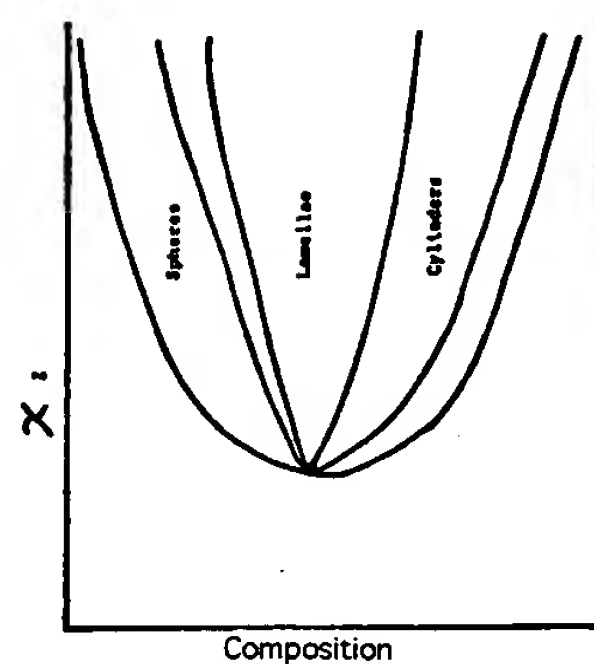


Figure 2. Diagram corresponding to a phase diagram for block copolymers.

First published: ACS Division of Polymeric Materials: Science and Engineering (PMSE), **74** (1996).